

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 10/00, 4/602		A1	(11) International Publication Number: WO 96/35729 (43) International Publication Date: 14 November 1996 (14.11.96)
(21) International Application Number: PCT/EP96/01941		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 9 May 1996 (09.05.96)		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(30) Priority Data: 95870048.6 9 May 1995 (09.05.95) (34) Countries for which the regional or international application was filed: EP 95870049.4 9 May 1995 (09.05.95) (34) Countries for which the regional or international application was filed: BE et al. EP 95870050.2 9 May 1995 (09.05.95) (34) Countries for which the regional or international application was filed: BE et al. EP			
(71) Applicant (for all designated States except US): FINA RESEARCH S.A. [BE/BE]; Zone Industrielle C, B-7181 Seneffe (BE).			
(72) Inventors; and (75) Inventors/Applicants (for US only): RAZAVI, Abbas [IR/BE]; Domaine de la Brisée 35, B-7000 Mons (BE). DEBRAS, Guy [BE/BE]; Rue Champ de la Chapelle 12, B-6210 Les Bons Villers (BE).			
(54) Title: PROCESS FOR PREPARING AND USING A SUPPORTED METALLOCENE-ALUMOXANE CATALYST			
(57) Abstract			
<p>A process for the preparation of supported metallocene-alumoxane catalysts comprising the steps of: a) reacting a metallocene with an alumoxane at a temperature comprised between 15 and 50 °C, b) recovering a mixture comprising an alkylmetallocenium cation and an anionic alumoxane oligomer, c) reacting said mixture with a support, and d) recovering a supported metallocene-alumoxane catalyst as a dry solid, the reaction with the support being carried out at a temperature comprised between 85 °C and 110 °C, preferably between 90 and 130 °C, and their use for the polymerization or copolymerization of olefins.</p>			

- 1 -

"Process for preparing and using a supported metallocene-alumoxane catalyst".

5 The present invention relates to a new process for preparing supported metallocene-alumoxane catalysts and their use in the polymerization or copolymerization of olefins.

10 Olefin (co)polymerization catalysts comprising a metallocene and an alumoxane have been known for a long time. European patent application n° 0 035 242 discloses a process for preparing ethylene and atactic propylene polymers in the presence of a halogen free cyclopentadienyl transition metal salt and an alumoxane.

15 The use of the homogeneous metallocene-alumoxane catalyst systems in the continuous olefin polymerization processes leads to several drawbacks. Indeed it invariably causes severe reactor wall fouling and crust formation, and further the resulting polymers are very fluffy and exhibit very low bulk densities.

20 In order to solve these problems, it was proposed to work with heterogeneous metallocene-alumoxane catalyst systems. For example these supported metallocene-alumoxane catalysts are described in European patent n° 0 619 325.

25 Known methods for preparing supported metallocene-alumoxane catalysts are disclosed in Makromol. Chem., Rapid Commun. 14, 239-243, 1993 (W. Kaminsky).

30 None of the above-mentioned patents and article reports about successful use (high activity, absence of reactor fouling) of any supported

- 2 -

metallocene-alumoxane catalyst for the polymerization or copolymerization of olefins.

US patent 5,240,894 relates to a process for producing a supported metallocene-alumoxane catalyst comprising forming an alumoxane-metallocene reaction solution, adding a porous support, evaporating the resulting slurry so as to remove residual solvent from the support and optionally prepolymerizing the catalyst with olefinic monomer. According to the description it is mentioned that the temperature maintained during reaction of the metallocene/alumoxane solution and support can be vary such as, for example, from 0°C to 100°C. However all the examples given mention reaction mixtures heated at temperatures not higher than 66°C. Experiments were carried out by the Applicant and showed that when the contact between the metallocene/alumoxane and the support is made at the temperatures exemplified the efficiency catalyst of the so obtained supported catalytic system in the polymerization or copolymerization of olefins is not sufficiently high for an industrial application and yet an important reactor fouling is formed.

One of the aims of the present invention is consequently to overcome the above-mentioned drawbacks and to provide a process for preparing a supported metallocene-alumoxane catalyst having a surprisingly high activity and low reactor fouling.

To this end, according to the present invention, said process which comprises the following steps :

- a) reacting a metallocene with an alumoxane at a temperature comprised between 15 and 50°C,
- b) recovering from step a) a mixture comprising an alkylmetallocenium cation and an anionic alumoxane oligomer,
- c) reacting said mixture with a support, and

- 3 -

d) recovering a supported metallocene-alumoxane catalyst as a dry solid,
is characterized in that the reaction of step c) is
carried out at a temperature comprised between 85°C and
5 110°C, preferably at a temperature comprised between 90
and 110°C, and most preferably at 110°C.

According to an advantageous embodiment of
the invention, the duration of the reaction of step c)
is between 60 and 120 minutes, preferably of about 90
10 minutes.

The invention also relates to a process for
the polymerization or copolymerization of olefins
comprising contacting at least one olefinic monomer in
the presence of a supported catalyst thus obtained.

15 Further details and features of the invention
will be evident from the description given below by
way of a non-limiting example of several particular
embodiments of the invention.

As has already been indicated above, the
20 supported metallocene-alumoxane catalysts of the invention
are obtained by

- a) reacting a metallocene with an alumoxane at a
temperature comprised between 15 and 50°C,
- b) recovering from step a) a mixture comprising an
alkylmetallocenium cation and an anionic aluminoxane
25 oligomer,
- c) reacting said mixture with a support, and
- d) recovering a supported metallocene-alumoxane as a
dry solid,

30 the reaction between the mixture metallocene-alumoxane
and the support being conducted at a temperature com-
prised between 85°C and 130°C, preferably between 90 and
110°C, most preferably at about 110°C. The duration of
said reaction is generally from about 1 to 2 hours,
35 preferably of the order of 90 minutes.

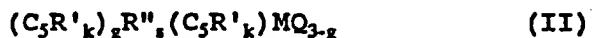
- 4 -

Any metallocene in the art known as suitable for the polymerization of olefins can be used in the present invention.

Preferred metallocenes including isomerizable metallocenes which can be racemic or not, are represented by the general formulae :



wherein Cp is a cyclopentadienyl ring, M is a Group 4b, 5b or 6b transition metal, R is a hydrocarbyl or hydrocarboxy group having from 1 to 20 carbon atoms, X is a halogen, and m = 1-3, n = 0-3, q = 0-3 and the sum of m+n+q will be equal to the oxidation state of the metal.



and



wherein $(C_5R'^k)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' is the same or different and is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical containing from 1 to 20 carbon atoms or two carbon atoms are joined together to form a C₄-C₆ ring, R'' is a C₁-C₄ alkylene radical, a dialkyl germanium or silicon or siloxane, or an alkyl phosphine or amine radical bridging two $(C_5R'^k)$ rings, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having from 1-20 carbon atoms, hydrocarboxy radical having 1-20 carbon atoms or halogen and can be the same or different from each other, Q' is an alkylidene radical having from 1 to about 20 carbon atoms, s is 0 or 1, g is 0, 1 or 2, l is 0 when g is 0, k is 4 when s is 1 and k is 5 when s is 0, and M is as defined above.

Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl

- 5 -

and the like. Exemplary halogen atoms include chlorine, bromine, fluorine and iodine and of these halogen atoms, chlorine is preferred. Exemplary hydrocarboxy radicals are methoxy, ethoxy, propoxy, butoxy, amyloxy and the
5 like. Exemplary of the alkylidene radicals are methylidene, ethylidene and propylidene. Among these one can cite

isopropylidene (cyclopentadienyl fluorenyl) (zirconium dichloride),
10 diphenyl methylidene (cyclopentadienyl fluorenyl) (zirconium dichloride),
(biscyclopentadienyl) (zirconium dichloride), and
(bismethylcyclopentadienyl) (zirconium dichloride).

More preferred metallocenes including
15 isomerisable metallocenes which can be racemic or not, are selected from bisindenyl compounds having the following formula :



wherein Ind is an indenyl or a substituted indenyl, R''
20 is a C₁-C₄ alkylene radical, a dialkyl germanium or silicon or siloxane, or an alkyl phosphine or amine radical bridging the indenyls, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms, hydrocarboxy radical having 1-20 carbon atoms or halogen and can be the same or different from each other, and M is
25 Ti, Zr or Hf. Among these one can cite
(bisindenyl) ethane (zirconium dichloride),
(bisindenyl) ethane (hafnium dichloride), and
30 dimethylsilyl (bisindenyl) (zirconium dichloride).

The term "isomerisable" means herein that the metallocene comprises different centres of chirality and has a flexible structure.

Any alumoxane known in the art can be used
35 in the present invention.

- 6 -

The preferred alumoxanes comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formulae :

5



for oligomeric, linear alumoxanes and



for oligomeric, cyclic alumoxanes,

10 wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C₁-C₈ alkyl group and preferably methyl. Generally, in the preparation of alumoxanes from, for example, trimethyl aluminium and water, a mixture of linear and cyclic compounds is obtained.

15 Methylalumoxane is preferably used. The alumoxane is usually delivered as a concentrated solution of alumoxane in toluene.

20 The support used in the present invention can be any organic or inorganic solids, particularly porous supports such as talc, inorganic oxides, and resinous support material such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided form.

25 Suitable inorganic oxide materials which are desirably employed in accordance with this invention include Group 2a, 3a, 4a or 4b metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins such as finely divided polyethylene. Preferably, the support is a silica having a surface area comprised between 200 and

- 7 -

600 m²/g and a pore volume comprised between 0.5 and 4.5 ml/g.

The reaction between the metallocene and the alumoxane (step a) is a multi-step equilibrium type reaction involving mono- and di- alkylation of the metallocene, mono-, di- or multi- metallic species and finally abstraction of an alkyl group, and formation of active cationic species. The reaction between the metallocene and the alumoxane is performed at a temperature comprised between 15 and 50°C, preferably about 25°C. The reaction is usually conducted in the presence of a solvent, preferably toluene.

The amount of alumoxane and metallocene usefully employed in the preparation of the solid support catalyst can vary over a wide range. Preferably, the aluminium to transition metal mole ratio is comprised between 1:1 and 100:1, preferably between 5:1 and 50:1.

The order of addition of the support to the mixture comprising the alkylmetallocenium cation - anionic alumoxane oligomer can be reversed. However, the mixture alkylmetallocenium cation - anionic alumoxane oligomer is added to the support material slurried in a suitable hydrocarbon solvent. Suitable solvents include mineral oils and the various hydrocarbons which are liquid at temperature and pressure conditions and which do not react with the individual ingredients. Illustrative examples of the useful solvents include the alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane, cycloalkanes such as cyclopentane and cyclohexane, and aromatics such as benzene, toluene, ethylbenzene, xylene and diethylbenzene, the preferred being toluene.

As above mentioned, the reaction between the support and the mixture alumoxane-metallocene is conducted at a temperature comprised between 85 and 130°C,

- 8 -

preferably between 90 and 110°C, most preferably around 110°C during a time period of 60 to 120 minutes, preferably of about 90 minutes.

Another advantage of the present catalyst
5 besides its high efficiency and low fouling is the facility and rapidity with which it is prepared. Indeed the process of the invention does not require the time-consuming washing steps of the prior art; the final catalyst system is prepared within 1-2 1/2 hours.
10 Further it does not require the consumption of large amounts of solvent which is needed in the most prior art methods.

According to the present invention, there is also provided a process for the polymerization or copolymerization of olefins comprising contacting one or more olefinic monomers in the presence of a supported metallocene-alumoxane catalyst prepared according to such a process. When an isomerisable metallocene or an isomerisable racemic metallocene component is used
15 bimodal olefin polymer or copolymers having a broadened molecular weight distribution with good processability, good physical properties and diverse applicability are obtained. As a matter of fact, broadening the molecular weight distribution is one way to improve the processing
20 of high molecular weight polyolefins, in applications requiring fast processing at fairly high die swell, such as in blowing and extrusion techniques.
25

The catalyst prepared according to the present invention can be used in gas, solution or slurry polymerizations. The polymerization process is preferably conducted under slurry phase polymerization conditions. The slurry phase polymerization conditions comprise usually a temperature of about 20 to 125°C and a pressure of about 0.1 to 5.6 MPa for a time between 10
30 minutes and 4 hours. It is preferred that the polymerization reaction be run in a diluent at a tem-
35

- 9 -

perature at which the polymer remains as a suspended solid in the diluent. Diluents include, for example, isobutane, n-hexane, n-heptane, methylcyclohexane, n-pentane, n-butane, n-decane, cyclohexane and the like.

5 A suitable diluent is isobutane.

Generally, a continuous reactor is used for conducting the polymerization. This continuous reactor is preferably a loop reactor. During the polymerization process, at least one monomer, the catalytic system and 10 a diluent are flowed in admixture through the reactor. Hydrogen can be used. When used, it is preferred that the relative amounts of hydrogen and olefin introduced into the polymerization reactor be within the range of about 0.001 to 15 mole percent hydrogen and 99.999 to 85 15 mole percent olefin based on total hydrogen and olefin present, preferably about 0.2 to 3 mole percent hydrogen and 99.8 to 97 mole percent olefin. The olefinic monomer that is used in the process of the present invention to produce a polyolefin is preferably selected from 20 ethylene and other higher alpha olefins, preferably olefins having from 3 to 10 carbon atoms including for example, 4-methyl-1-pentene. More preferably these olefins are selected from the group consisting of ethylene, propylene, hexene, and mixtures thereof, 25 ethylene being the most preferred.

While alumoxane can be used as cocatalyst, it is not necessary to use alumoxane as cocatalyst during the polymerization procedure for preparing polyolefins according to the process of the present 30 invention. Further, the use of alumoxane as a cocatalyst during the polymerization may lead to the fouling of the reactor. One or more aluminiumalkyl represented by the formula AlR_x can be used, each R being the same or different and being selected from halides or from alcoxy 35 or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable aluminiumalkyl are

- 10 -

trialkylaluminium selected from trimethylaluminium, triethylaluminium, triisobutylaluminium, tri-n-octylaluminium or tri-n-hexylaluminium, the most preferred being triisobutylaluminium.

5 The invention will now be further described by the following non limiting examples.

Examples

1. Catalyst preparation (Examples A₁ to A₆)

10 The support used is a silica having a total pore volume of 4.217 ml/g and a surface area of 322 m²/g. This silica is further prepared by drying in high vacuum on a schlenk line for three hours to remove the physically absorbed water. 5 g of this silica are suspended in 50 ml of toluene and placed in a round 15 bottom flask equipped with magnetic stirrer, nitrogen inlet and dropping funnel.

An amount of 0.31 g of isomerisable metallocene is reacted with 25 ml of methylalumoxane (MAO 30 wt% in toluene) at a temperature of 25°C during 20 10 minutes to give a solution mixture of the corresponding metallocenium cation and the anionic methylalumoxane oligomer.

25 Then the resulting solution comprising the metallocenium cation and the anionic methylalumoxane oligomer is added to the support under a nitrogen atmosphere via the dropping funnel which is replaced immediately after with a reflux condenser. The mixture is heated to 110°C for 90 minutes. Then the reaction mixture is cooled down to room temperature, filtered 30 under nitrogen and washed with toluene.

The colour of the filtrate indicates if the fixation of the cation is quantitative. A colourless filtrate usually means a complete fixation. The catalyst obtained is then washed with pentane, dried under a mild 35 vacuum and recovered as a solid dry free flowing powder. The type of metallocene, the temperature and the time

- 11 -

period of the reaction between the mixture alumoxane-metallocene and the support, the colour of the filtrate and the amount of catalyst obtained are given in Table 1 hereafter.

5 2. Polymerization procedure

Examples 1 to 10

Three minutes before the introduction of the catalyst into the reaction zone 1 ml of 25 wt% of triisobutylaluminium (TIBAL) in toluene is added to the 10 catalyst.

All polymerizations were performed in a four liters bench reactor. For the polymerization of ethylene the reactor contains two liters of isobutane as diluent (Examples 1 to 6, 9 and 10). For the polymerization of propylene, the diluent is propylene (Examples 7 and 8). The catalyst type, the polymerization conditions and the polymer properties are given in Table 2 hereafter. As indicated in Table 2, some examples include a prepolymerization step which consists of the introduction of 15 the catalyst of 30°C and a heating until the polymerization temperature. 20

- 12 -

Table 1

Example	Silica (g)	Metallocene		MAO (ml)	T (°C)	Time (min)	Filtrate	Catalyst (g)
		Type : isomerisable	(g)					
A1	5	Ind ₂ EtZrCl ₂	0.31	25	110	90	colourless	8.2
A2	5	Ind ₂ (Me ₂ Si)ZrCl ₂	0.31	25	110	90	colourless	10
A3	5	Ind ₂ EtZrCl ₂	0.31	25	110	90	colourless	8.6
A4	5	Ind ₂ EtHfCl ₂	0.31	25	110	90	colourless	7.5
A5	5	iPrCpFluZrCl ₂	0.31	25	110	90	colourless	8.6
A6	5	Ph ₂ CCpFluZrCl ₂	0.31	25	110	90	colourless	7.6

Ind₂EtZrCl₂ (bisindenyl) ethane (zirconium dichloride)
 Ind₂(Me₂Si)ZrCl₂ dimethylsilyl (bisindenyl) ethane (zirconium dichloride)
 Ind₂EtHfCl₂ (bisindenyl) ethane (hafnium dichloride)
 iPrCpFluZrCl₂ isopropylidene (cyclopentadienyl fluorenyl) (zirconium dichloride)
 Ph₂CCpFluZrCl₂ diphenyl methylidene (cyclopentadienyl fluorenyl) (zirconium dichloride)

- 13 -

In all examples, the mixture alkylmetallo-cenium cation-anionic alumoxane oligomer has been added to the support material except for Example A3 where the order of addition has been reversed.

- 14 -

Table 2

Ex.	Catalyst		Prepolymerization (Yes/no)(C*)	Polymerization		Monomer		Hydrogen (NI)	Hexene (wt %)	Yield (g)	Activity (g/g·h)	Bulk (1)	MI (2)	HLMI (3)
	(mg)	Type		T (°C)	Time (min)	Type	(wt %)							
1	100	A.2	NO	2.2	80	60	C ₂	6	0.25	2.44	301	0.42	7.08	287.2
2	100	A.2	YES/30	2.2	80	60	C ₂	6	0.5	2.44	506	0.41	0.03	9.1
3	100	A.2	YES/30	2.3	90	60	C ₂	6	0.25	1.22	490	0.40	0.13	17.07
4	100	A.2	YES/30	2.3	90	60	C ₂	6	0.5	1.22	488	0.44	0.08	12.24
5	100	A.3	YES/30	2.3	90	60	C ₂	6	0.25	1.22	430	0.42	ND	ND
6	100	A.4	NO	2.3	90	90	C ₂	6	0.25	1.22	365	2433	0.42	3.57
7	100	A.5	YES/30	2.5	60	60	C ₂	100	0	0	36	ND	ND	ND
8	100	A.5	YES/30	3.0	70	60	C ₂	100	0	0	15	ND	ND	ND
9	100	A.1	NO	2.4	70	60	C ₂	6	0	0	160	1600	0.28	0.02
10	100	A.2	NO	2.3	90	60	C ₂	6	0	0	78	780	0.24	2.8
														2.4

C₂: ethylene
C₃: propylene

(1) Bulk density (ASTM-D-1895)

(2) Melt Index (ASTM-D-1238-89A)

(3) High Load Melt Index (ASTM-D-1238-89A)

- 15 -

Examples 11 to 14

The polymerization is carried out slurry in
a liquid full loop reactor. Ethylene is injected with
1-hexene together with the catalyst. Isobutane is used
5 as diluent. The catalyst type, polymerization conditions
and properties are indicated in Table 3.

The polymers were analyzed by Gel Permeation
Chromatography (GPC-WATERS MILLIPORE) and Differential
Scanning Calorimetry (DSC). The graphs are given in
10 Figures 1 to 4 respectively correspond to Examples 11
to 14 of Table 3). "D" represents the ratio M_w/M_n (MWD),
"D'" the ratio M_z/M_w and "A" the area under the curve.

- 16 -

Table 3

Reactor	11	12	13	14
Catalyst (type)	A2	A2	A1	A1
Reactor Vol (l)	70	70	70	70
T (°C)	80	80	80	80
C ₂ (kg/h)	5	4	8	7.5
C ₆ (cc/h)	400	376	325	300
H ₂ (Nl/h)	1.5	1.5	2	4
iC ₄ (kg/h)	20	20	30	30
PE resid. time (min)	60	60	60	60
TiBAL (ppm)	200	200	400	400
M12 (g/10')	0.02	0.035	0.053	0.14
HLMI (g/10')	3.93	5.5	7.7	16.3
Density (g/cc)	0.933	0.931	0.937	0.942
Bulk density (g/cc)	0.44	0.44	0.44	0.42
MWD	6.2	8.1	6.4	7.0

C₂ : ethylene
 C₆ : 1-hexene
 iC₄ : isobutane
 TiBAL : triisobutylaluminium
 Bulk density : Melt Index
 M12 : HLMI : High Load Melt Index

(ASTM-D-1985)
 (ASTM-D-1238-89A)
 (ASTM-D-1238-89A)

- 17 -

Examples 15 to 20

These examples (Table 4) show the surprising and very important role of the temperature of the reaction between the mixture metallocene/MAO and the support on the catalyst efficiency in the polymerization of ethylene. In Examples 15 to 18 (prior art) the reaction has been conducted at a temperature from 20 to 70°C during time periods from 2 hours to about 48 hours, thus within the range of the temperatures cited in the examples of US patent n° 5,240,894 and in Examples 19 and 20 (invention) at 90°C, a temperature according to the present invention. As shown the activity of the catalyst of Example 19 is substantially the same as for Examples 15 to 18 but for a time period twice as short whereas the activity of the catalyst of Example 19 is substantially higher. Further in the examples of the prior art important fouling is formed in the reactor.

Table 4

Example	MAO (ml)	$\text{Ind}_2\text{EtZrCl}_2$ (g) ^(a)	Addition order ^(b)	T (°C)	Time (min)	Filtrate	Activity (g/g.h)	Fouling
15	50	6.3	(2 + tol) + 1	20	120	yellow	3000	important
16	50	6.3	1 + (2 + tol)	20	120	yellow	1380	important
17	50	6.3	1 + (2 + tol)	60	120	yellow	1280	important
18	25	6.0	1 + 2	70	120	pale yellow	1560	important
19	25	6.3	1 + 2	90	60	yellow	1540	weak
20	25	6.3	1 + 2	90	120	colourless	5820	weak

(a) Amount in wt% with reference to initial silica.

(b) 1 : silica (Grace 955) + toluene

2 : metallocene + MAO (30 wt% sil in toluene WTiCO)

1 + 2 : (silica/toluene) + (metallocene/MAO)

2 + 1 : (metallocene/MAO) + (silica/toluene).

- 19 -

CLAIMS

1. A process for the preparation of a supported metallocene-alumoxane catalyst comprising the steps of :
 - 5 a) reacting a metallocene with an alumoxane at a temperature comprised between 15 and 50°C,
 - b) recovering from step a) a mixture comprising an alkylmetallocenium cation and an anionic alumoxane oligomer,
 - 10 c) reacting said mixture with a support, and
 - d) recovering a supported metallocene-alumoxane catalyst as a dry solid,
characterized in that the reaction of step c) is carried out at a temperature comprised between 85°C and 130°C.
- 15 2. A process according to claim 1 wherein said temperature is comprised between 90°C and 110°C.
3. A process according to claim 2 wherein said temperature is of 110°C.
4. A process according to any one of claims 1
20 to 3 wherein the duration of the reaction of step c) is between 60 and 120 minutes.
5. A process according to claim 4 wherein said duration is of about 90 minutes.
6. A process according to any one of claims 1
25 to 5 wherein the metallocene is an isomerisable component.
7. A process according to claim 6 wherein the isomerisable metallocene is a racemic component.
8. A process according to either of claims 6
30 and 7 wherein the metallocene is selected from bis-indenyl compounds having the formula :



wherein Ind is an indenyl or a substituted indenyl, R'' is a C₁-C₄ alkylene radical, a dialkyl germanium or silicon or siloxane, or an alkyl phosphine or amine

- 20 -

radical bridging the indenyls, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms, hydrocarboxy radical having 1-20 carbon atoms or halogen and can be the same or different from each other, and M is 5 Ti, Zr or Hf.

9. A process according to claim 8 wherein the metallocene is

(bisindenyl) ethane (zirconium dichloride),
10 (bisindenyl) ethane (hafnium dichloride), or
dimethylsilyl (bisindenyl) (zirconium dichloride).

10. A process according to either of claims 6 and 7 wherein the metallocene is
isopropylidene (cyclopentadienyl fluorenyl) (zirconium dichloride),
15 diphenyl methyldene (cyclopentadienyl fluorenyl) (zirconium dichloride),
(biscyclopentadienyl) (zirconium dichloride), or
(bismethylicyclopentadienyl) (zirconium dichloride).

20 11. A process according to any one of claims 1 to 10 wherein the alumoxane is methylalumoxane.

12. A process according to any one of claims 1 to 11 wherein the support is a silica having a surface area comprised between 200 and 600 m²/g and a pore 25 volume comprised between 0.5 and 4.5 ml/g.

13. A process according to any one of claims 1 to 12 wherein the catalyst is recovered as a free flowing powder.

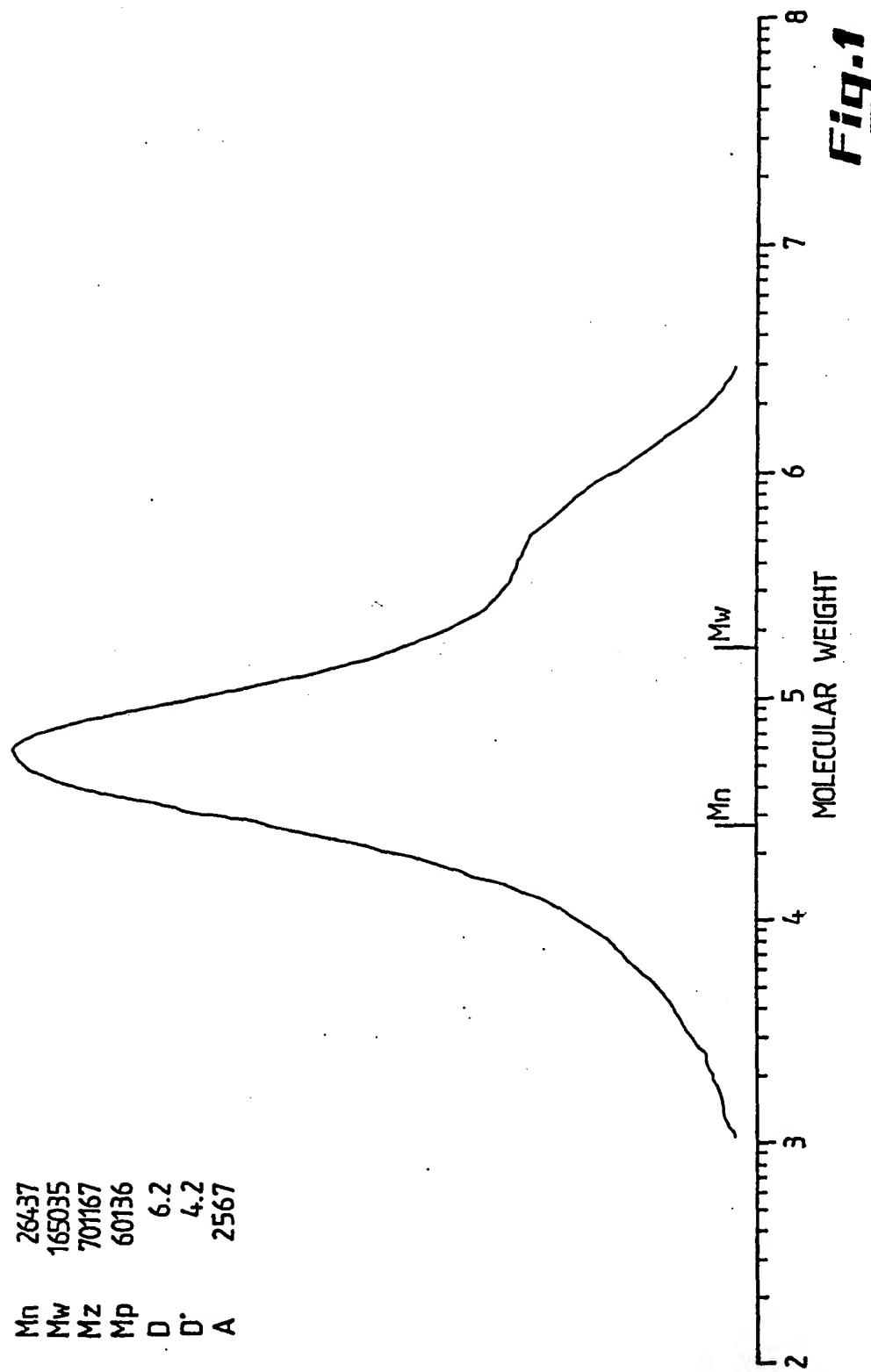
30 14. A process for the polymerization or copolymerization of olefins comprising contacting at least one olefinic monomer in the presence of a supported catalyst such as prepared according to any one of claims 1 to 13.

35 15. A process according to claim 14 wherein the olefinic monomer is ethylene or propylene.

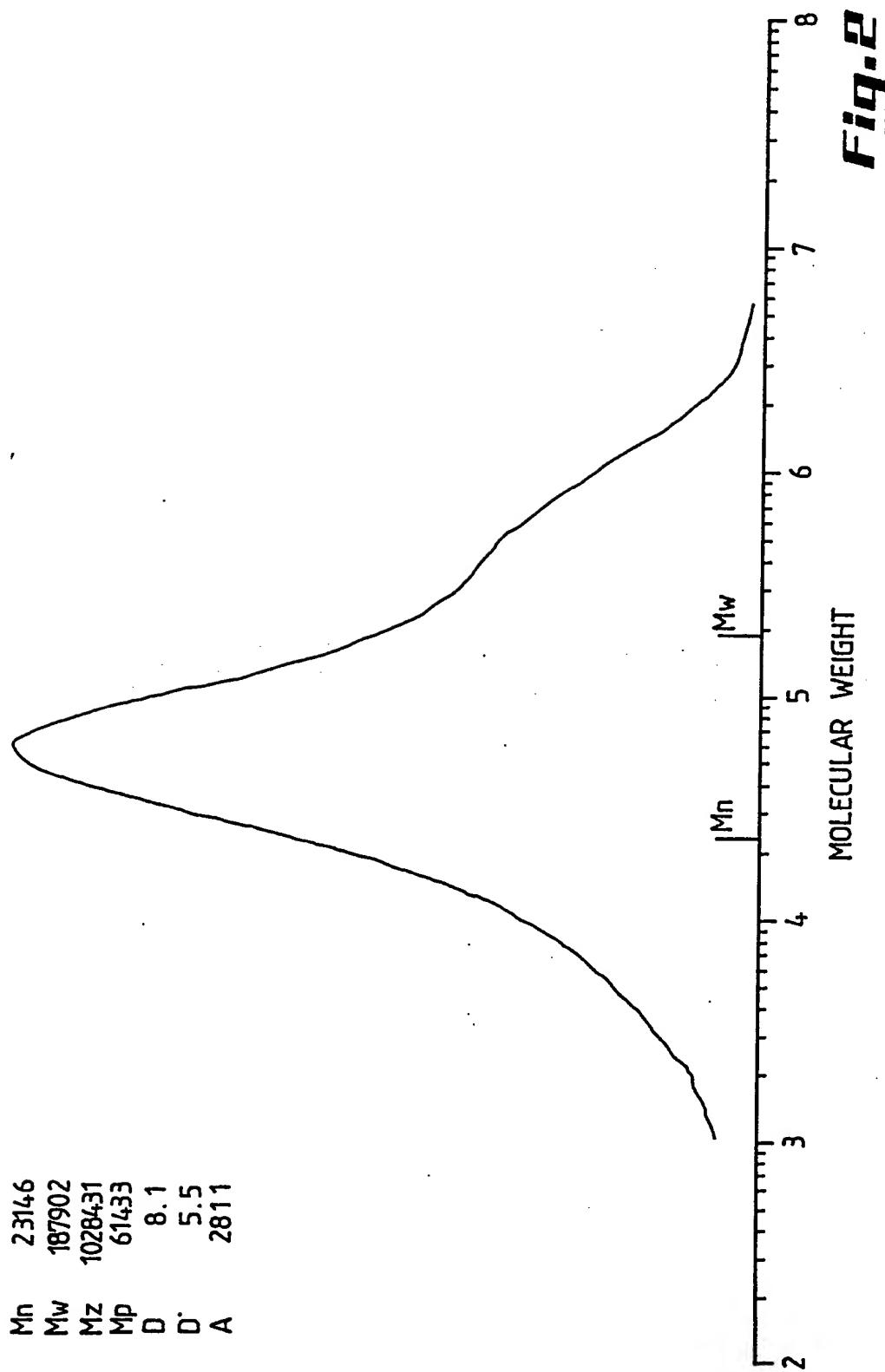
- 21 -

16. An olefin polymer or copolymer with a broad and bimodal molecular weight distribution such as obtained by the process according to claim 14.

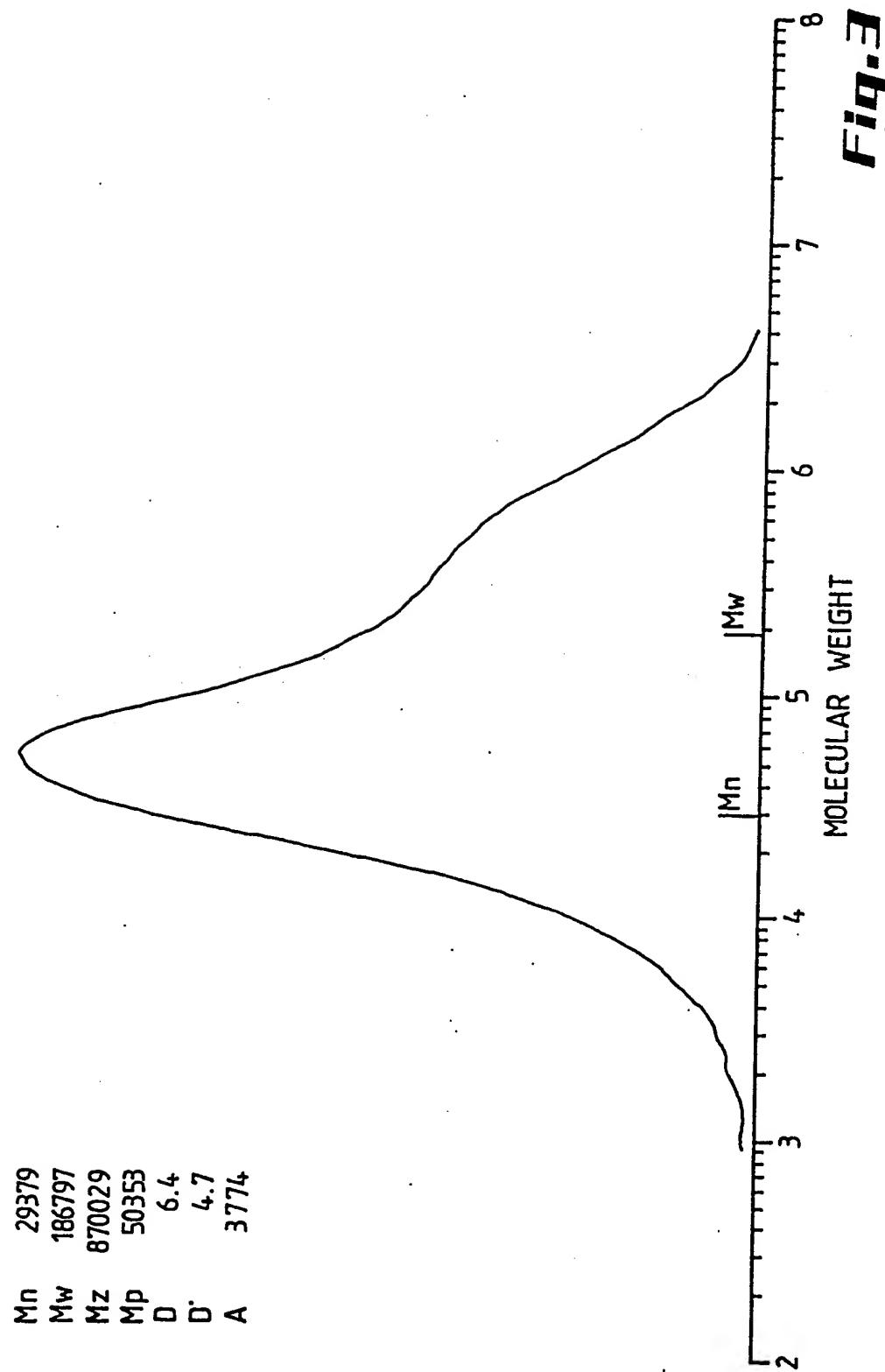
1 / 4



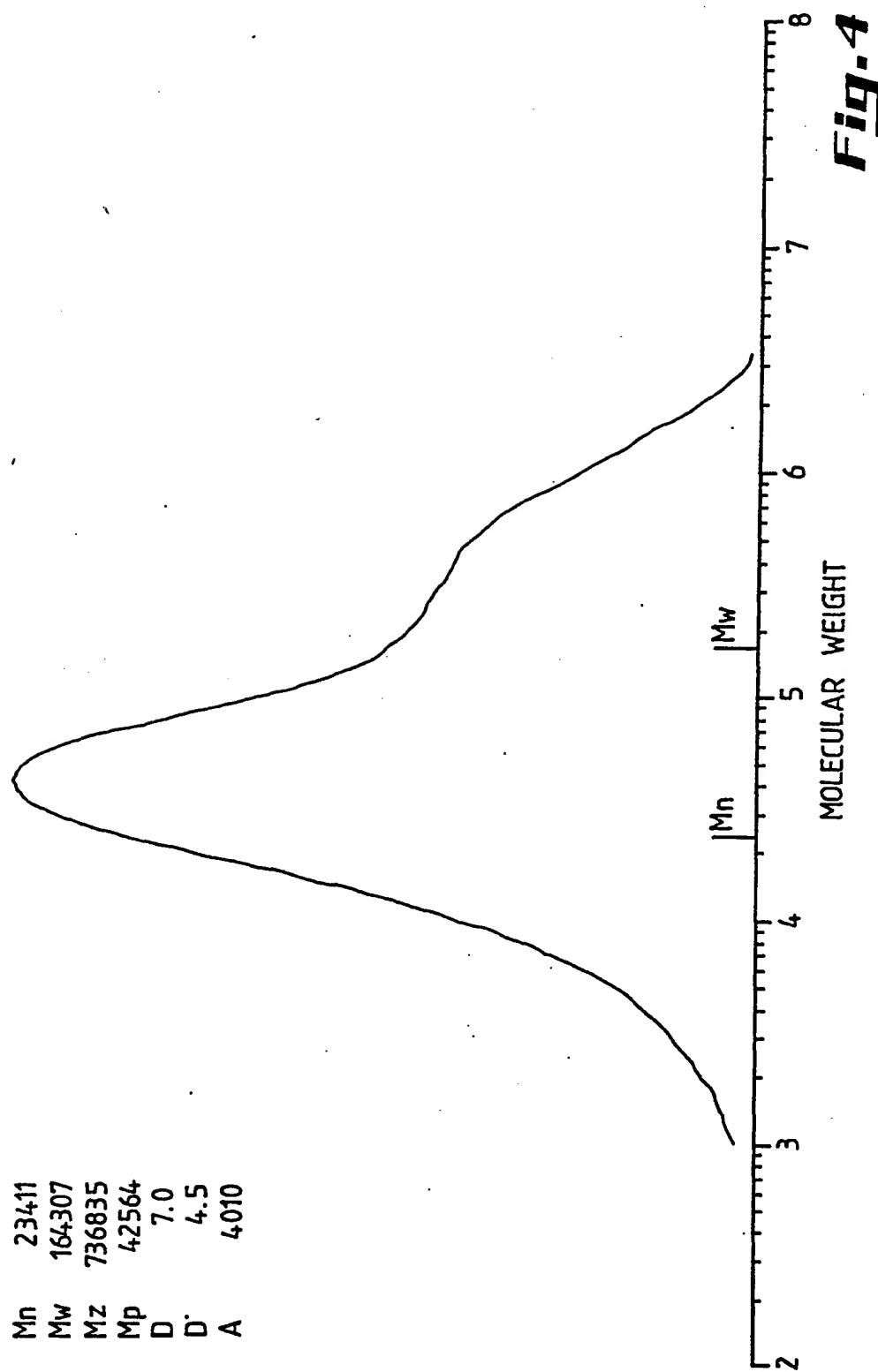
2 / 4



3 / 4



4 / 4



INTERNATIONAL SEARCH REPORT

Inten
Application No
PCT/EP 96/01941

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F10/00 C08F4/602

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 240 894 (BURKHART TERRY J.) 31 August 1993 see examples 1,5,9 see column 6, line 24 - line 50 see claim 1 ---	1,2,4, 6-8,10, 11,14,15
Y	WO,A,96 00243 (EXXON) 4 January 1996 see example 1 see page 9, line 31 - page 10, line 9 ---	1,12,13
P,Y	EP,A,0 518 092 (BASF AKTIENGESELLSCHAFT) 16 December 1992 see claim 1 see example 1 see page 4, line 13 - line 34 ---	1,12,13
A	-/-	1,14,15

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

2

Date of the actual completion of the international search

2 September 1996

Date of mailing of the international search report

25.09.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentdienst 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Fischer, B

INTERNATIONAL SEARCH REPORT

Inten Application No
PCT/EP 96/01941

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 563 917 (HOECHST AKTIENGESELLSCHAFT) 6 October 1993 see claim 1 see example 1 see page 13, line 25 - line 44 ---	1,13,15
A	EP,A,0 586 167 (BP CHEMICALS) 9 March 1994 see examples 19,20 -----	1,13-15

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte... national application No

PCT/EP 96/01941

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-5240894	31-08-93	CA-A-	2135998	25-11-93
		EP-A-	0642536	15-03-95
		JP-T-	7508065	07-09-95
		WO-A-	9323439	25-11-93
WO-A-9600243	04-01-96	AU-B-	2870295	19-01-96
EP-A-518092	16-12-92	DE-A-	4119343	17-12-92
		JP-A-	5140226	08-06-93
EP-A-563917	06-10-93	AU-B-	3559893	07-10-93
		CA-A-	2093056	02-10-93
		JP-A-	6025348	01-02-94
		ZA-A-	9302305	18-10-93
EP-A-586167	09-03-94	CA-A-	2105015	05-03-94
		CN-A-	1087096	25-05-94
		FI-A-	933805	05-03-94
		JP-A-	6172415	21-06-94
		NO-A-	933078	07-03-94